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ADSORPTION DESULFURIZATION OF GAS-OIL ON TO IRAQUI ATTAPULGITE AND BENTONITE IMPREGNATED WITH TiO_2, ZnO AND MoO_3

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ABSTRACT

Desulfurization of gas-oil was investigated. The adsorption desulfurization process was carried out on a highly efficient agents using various Clay Mineral (CM) (Attapulgite and Bentonite), which were brought from western Iraqi desert. Desulfurization processes were investigated using applying three temperatures (400, 500 and 550 ^{0}C) and three kinds of catalysts: firstly CM only, secondly CM + (TiO_2 or ZnO or MoO_3) and thirdly Nano CM, by additive 5, 15 and 25% of minerals oxides both separately. TGA have shown the thermal stability of Clay and X-ray was used for measurement the conversion% of sulfurs, which were (0.95 to 0.47) using Attapulgite, (0.95 to0.54) using Bentonite , (0.95 to 0.45) using Attapulgite + 25% TiO_2, (0.95 to 0.34) using Nano Bentonite + TiO_2 and ,(0.95 to 0.29) using Nano Attapulgite + 25%TiO_2 which was the best. Desulfurization results. Which retleching the good performance of the used catalyst. Gas Chromatography (GC) techniques is used to follow-up Dibenzotiophene (DBT) which is a compound in gas-oil.

Keywords: Desulfurization, Attapulgite , Bentonite , Gas-oil, Catalyst,

INTRODUCTION

In the process of combustion, sulfur-containing compounds are converted into sulfur oxides (SOx), which are known to poison the noble-metal catalysts used in automobiles as well as contribute to acid rain and other forms of environmental pollution. This makes sulfur-containing compounds one of the most prevalent contaminants found in transportation fuels. As a consequence of this, environmental regulations all over the world are becoming increasingly stringent in order to limit the levels of sulfur in transportation fuels [1]. The poor quality of crude oil that is currently available can clearly be expected to result in the high sulfur contents of oil products, which can lead to corrosion, catalyst poisoning, and other undesirable outcomes [2]. In recent years, one of the most pressing concerns in the industry has been the elimination of sulfur compounds from liquid fuels. This is not only because of increasingly stringent environmental regulations, but also because of the proliferation of fuel cell applications. The level of sulfur in the product must be reduced to less than 0.1 ppm [3] because sulfur compounds in fuels are a major source of pollution, and because containing compounds such as thiophenes can poison catalysts used to remove the residue of hydrocarbons and nitrogen oxides derived from combustion reactions, sulfur compounds in fuels are a major contributor to air pollution [4]. The current caustic washing method for oil desulfurization is one of the current technologies for desulfurization of crude oil. The dry gas desulfurization method, hydrodesulfurization (HDS), oxidative desulfurization (ODS), and biodesulfurization are the four different types of desulfurization processes (BDS) [5]. Removal of organosulfur compounds by extraction or adsorption is economically viable and simple in operation. To meet

the needs for producing clean fuels, decreasing the sulfur content of crude oil becomes an urgent task [6]. Both gasoline and diesel sold in stores have high levels of organic sulfur compounds, with concentrations ranging between 300 and 500 parts per million (ppm) (parts per million by weight). These sulfur compounds that are present in the fuel oils have the potential to cause serious pollution to the environment because, when they are burned, they will transform into SOx species [7]. During the phase of oil processing that involves sulfur compounds, this also causes severe corrosion of the reactors and other equipment. An alternative technology that has been reported involves the desulfurization of commercial fuels through the use of selective adsorption . Sun, L., Song, C.S., Mehdi, [8]. Penelop Baltzopoulou, Kyrivakos X. Kallis. [9]. Kim: J. H.,Song,C [10]. Wang, J. Mei, Z.J. [11]. However, the sulfur adsorption capacity depends on the composition of the fuel. Adsorptive removal of sulfur compounds from liquid commercial fuels has been widely investigated using various different adsorbents such as porous carbon materials, metal impregnated oxides, zeolite Y of various metal cat ion forms. Natural Clay, Micro and Nano sized particles used as adsorbent for removal of organic compounds from oil such as organ-sulfurs. Nano Clay are extensively studied as new adsorbents with large surface area and small diffusion resistance for the separation and removal of chemical species. Different types of Clay minerals using as absorbents. Adsorption desulfurization is a relatively new technique that has proven to be very effective in removing sulfur compounds from fuels used for transportation. In addition, adsorption desulfurization can be carried out even under conditions of ambient pressure and temperature, which are relatively lower than those required by other methods [12].

The objective of the present investigation is to develop an improved process for the desulfurization of Gas-oil, using natural Clay as catalyst of absorbent and also activated that was impregnated with TiO_2, ZnO and MoO_3. And examine its activity for adsorption desulfurization and the present study also reports the effect of metal salts on the adsorbent capacity. Efficiency of Nano catalyst for adsorption process has been studied.

MATERIALS AND METHODOLOGY

Materials:

Diesel oil was collected locally from Baiji refinery. The main physical properties of the diesel oil are shown in Table (1). Clay Minerals (Bentonite - B, Attapulgite - A) collected from Rutba area / Iraq . Table (2). Shown the components of Clay.

Table.1. Physical properties of Gas-oil (Baiji)

TEST	METHOD	SPECIFICATION
SP.GRAVITY/ 15.6 °C	D-1298	0.84 MAX
A.P.I GRAVITY	___	37.0 MIN
COLOUR ASTM	D-1500	2.0 MAX
FLASH POINT (P.M) °C	D-93	54.0 MIN
VISCOSTY/40 °C	D-445	5.0 MAX
POUR POINT / °C	D-97	-9.0 MAX
SULFUR CONTENT WT%	D-1266	1.2 MAX - 0.75 MIN

CETANE INDEX CALCULATED	D-976	53.0 MIN
DIESEL INDEX	IP-21	55.0 MIN

Table.2. Constituent oxides of Clays

Bentonite		Attapulgite
Oxides	Weight %	Weight %
SiO_2	56.7	44.2
Al_2O_3	15.7	11.9
Fe_2O_3	5.12	4.7
CaO	4.5	10.6
MgO	3.4	4.7
Na_2O	1.1	0.9
K_2O	0.6	…….
SO_3	…….	2.3
L.O.I	9.5	15.8

Preparation of adsorbent:

Four types of adsorbent Clay mineral (CM) were used in this study; CM samples were washed with tap water to remove the impurities' materials and also washed with de-ionized water that can form during activation. The washed CM was dried at $80C^0$ for 24h in an oven to remove residual water. CM -1 Sample with will - physical activation (thermally activation) processes were carried out by dried MG in a muffle furnace ignition starting at 200^0C for an hour , $400c^0$ for another hour and finally at 600^0C for three hours then kept till usage.
MG- 2 (CM/ TiO_2), CM-3 (CM/ ZnO). and CM- 4 (CM/ MoO_3) were eventually impregnated with metal oxides at (5,15 and 25%). First, metal oxides which were dissolved in an HCl solution. Then, the each metal oxides solution was added to the sample of dried CM and maintained at ambient conditions for 3h to allow the absorbent to age and ground into small particles were activated with ignition under atmospheric air for 3hrat at 600^0C.

Thermal analysis:

Thermal Gravimetric Analysis (TGA) technique was used to analyses thermally
For CM, Kind 4000 - Perkin Elmer (USA), in Ibn-Sina Lab.(Baghdad).

Adsorption desulfurization method:

Desulfurization processes were carried out in a 100 mL flask diesel oil content of (0.954% of Sulfurs) was heated until boiling and then push a stream of air to assist the gas phase of gasoil to pass through 20cm of tubular quarts reactor, with an of internal diameter 1cm which filled with 20gm of activated CM- micro particles as adsorbent in furnace which is locally made Fig(1). Then the sweet gas-oil liquid products was recovery with a condenser and collected in a receiver flask. The side product of H_2S gas was precipitate as a yellow CdS

through flask which content of $CdCl_2.6H_2O$ solution. Processes were investigated using three temperatures (400, 500 and 550^0C).

Analytical methods:

The analytical methods were carried out by a Gas Chromatography (GC- FID) kind PACKARD MODEL 433A(USA) . And detector kind FID, detector temperature 300^0C, the temperature of the injection port $270C^0$, furnace temperature 100 – 300 ^{0}C and column kind SE / 30, 0 ^{0}C / min with capillary column (DB-5, 3M , diameter 1/ 8 , helium (He) used as the carrier gas of samples and flow rat 20m/ min. Spectroscopic charts of GC was recorded for the studied samples. The desulfurization products were determined by XR (thermo electronic) analyses was used for determinate the S% conversion quality control laboratory (Beji refinery).

Desulfurization tests for Nano size Clay:

The CM samples were ground and sieved by 30µm then washed with demineralized water for 2 times. Iron oxide were removed by sedimentation technique using 1M of NaOH solution under reflux for 2h at 100^0C. After filtration, the solid was exposed to slow evaporation, till the dryness was obtained.

2.50g N-acetyl-N,N,Ntrimethyl ammonium bromide CTAB was selected as surfactant to widen gallery spacing, was dissolved in 60 ml of distilled water containing 3.90×10^{-3} g mol of hydrochloric acid. The mixture was stirred under sonication at 75 ^{0}C during 30 min until a clear solution was obtained, thus indicating a perfect dissolution of ammonium salt. 3.25 g of CM was added to salt solution and sonication was continued for another 1 h. The precipitate formed was recovered by filtration and dispersed in hot water by mechanical stirring during 2 h the later process was repeated twice to get chloride free Nano clay. The final precipitate was thoroughly dried in an oven at 80 ^{0}C for 12 h, [13] . (AFM) Microscopy USA was used to determine for the Nano size to CM particles. Nano Clay desulfurization procedure is similar as above CM- micro particles methods of desulfurization

RESULTS AND DISCUSSION

Adsorptive desulfurization:

General three classes of absorbents (laboratory prepared) were used in this study for the desulfurization: Firstly direct desulfurization with CM only, secondly the desulfurization have been done with CM + Metal Oxide and thirdly desulfurization using Nano CM + TiO_2. All experimental carried out through home building reactor. Fig.1.

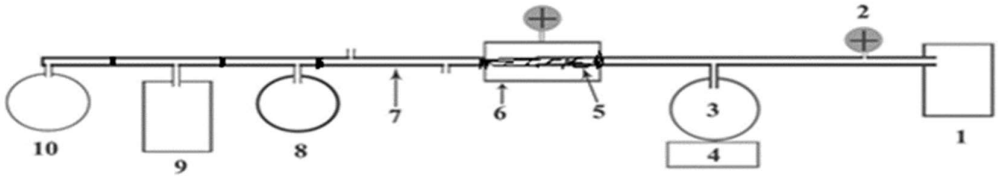


Fig.1. Schematic diagram of experimental apparatus. (1-Air Pump,2-flow meter, 3 – Feeding flask of virgin Gas-oil, 4- Heater, 5- Quarts reactor, 6 –Tubular furnace, 7 – condenser, 8 – Receiver flask of Sweet Gas-oil, 9- Cadmium chloride solution for Sulfur precipitate, 10 - H_2O flask for gases dissolve.

The regenerability of the adsorbents was tested by carrying out repeated adsorption–thermal regeneration cycle tests. In these sets of experiments, for each adsorbent, the adsorption run was performed at a fixed conditions of temperature (400,450 and 500^{0}C). The optimized temperature for high adsorption was 450^{0}C, and the best adsorbents is (Nano Attapulgite A + 25% TiO_2). The temperatures orders for the sulfurs removals ewre 450 °C > 400 °C > 500 ^{0}C. Results of desulfurization in Table (3- 7) by using Attapulgite – A and Bentonite – B. Fig.(2-9), and Fig.(13, 14).

Table.3 Adsorptive desulfurization using CM only.

Sample	Tempt. ^{0}C	B-CM	A-CM
Before desulfurization	**R.M**	**0.95 %**	**0.95 %**
After desulfurization	**at 400 °C**	**0.63**	**0.58**
	at 450 °C	**0.54**	**0.47**
	at 500 °C	**0.67**	**0.71**

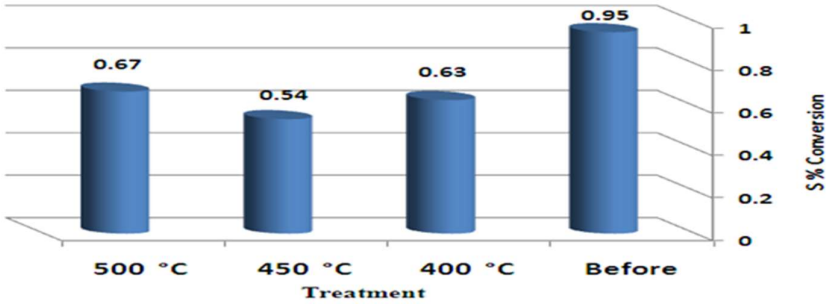


Fig.2. Desulfurization % using B- CM

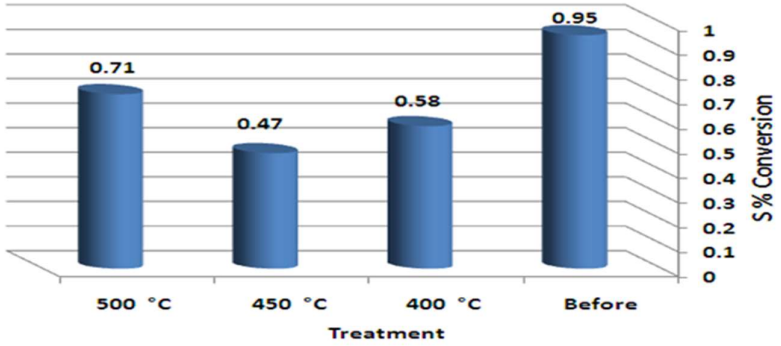


Fig.3. Desulfurization % using A-CM

Table.4 Adsorptive desulfurization results of CM+ TiO_2

CM	Tempt.C^0	5% TiO_2	15% TiO_2	25% TiO_2	Nano + 25% TiO_2
B	450	0.67	0.679	0.633	0.34
A	450	0.57	0.61	0.45	0.29

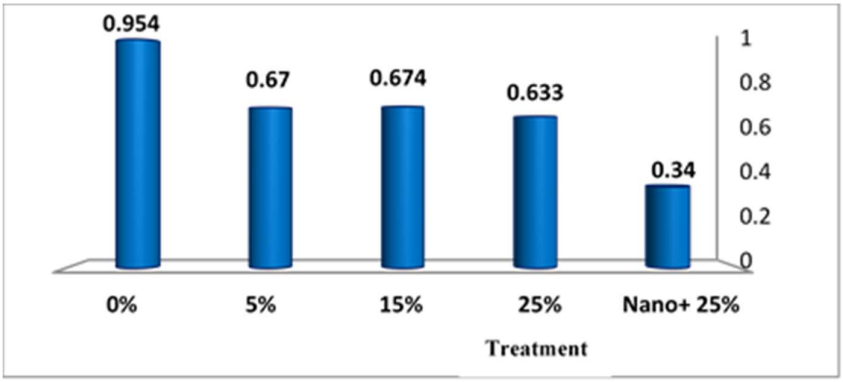


Fig.4. Relationship between B+ %TiO_2 and desulfurization

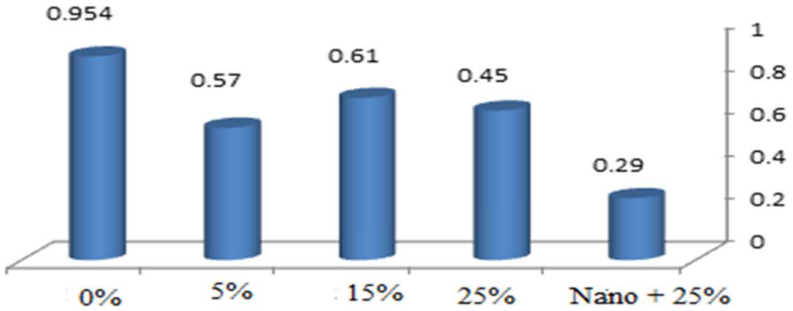


Fig.5. Relationship between A+ %TiO_2 and desulfurization

Table.5 Adsorptive desulfurization results of CM+ ZnO

CM	Tempt.C^0	5% ZnO	15% ZnO	25% ZnO
B	450	0.63	0.68	0.74
A	450	0.51	0.58	0.66

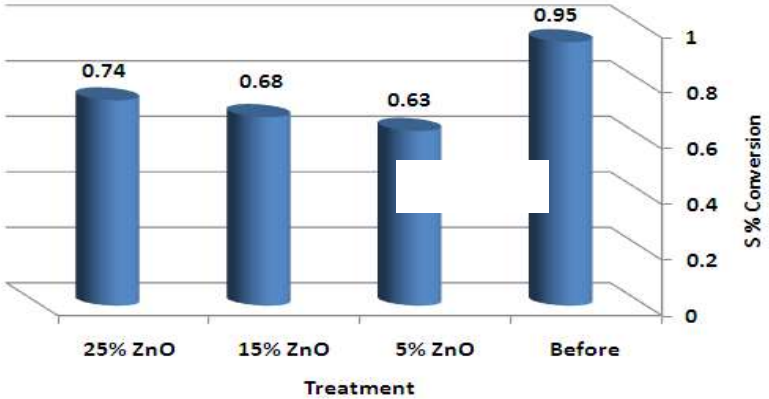


Fig.6. Relationship between B+ ZnO and desulfurization

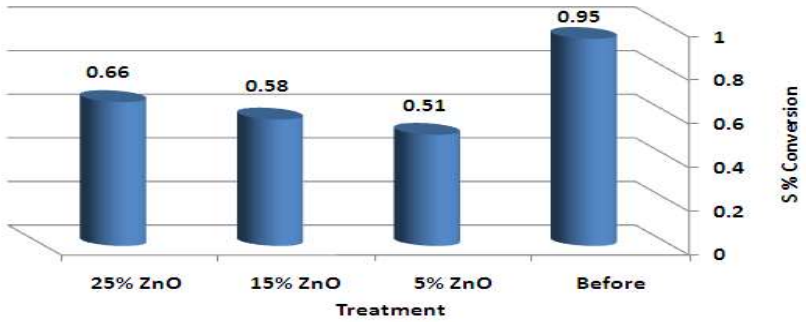


Fig.7. Relationship between A+ ZnO and desulfurization

Table.6 Adsorptive desulfurization results of CM + MoO_3

CM	Tempt.C^0	5% MoO_3	15% MoO_3	25% MoO_3
B	450	0.67	0.73	0.76
A	450	0.74	0.75	0.77

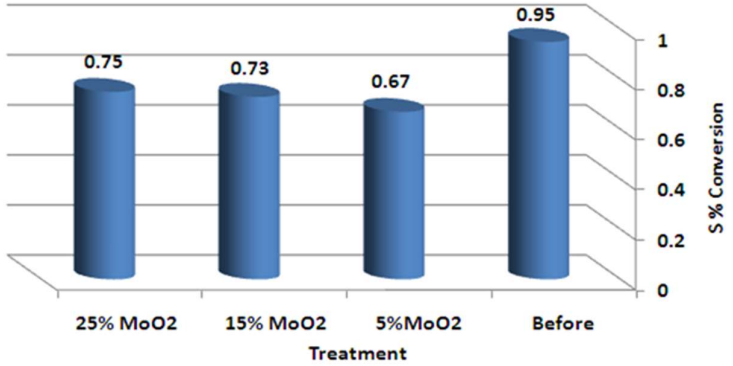
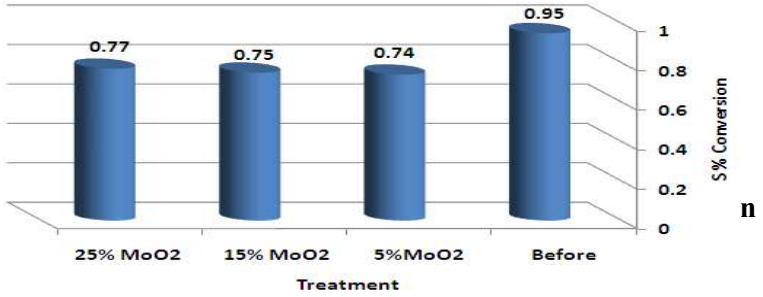


Fig.8. Relationship between B+ MoO_3 and desulfurization



n

To test the efficing of the adsorbents catalysts for sulfur removal from gas-oil, the high capacities for these adsorbents was of (Nano A+ TiO_2) and their favorites to sulfur removal. And show mechanism which suggested for adsorption desulfurization Fig.10.and image of Nano Clay, Fig. (11-12)

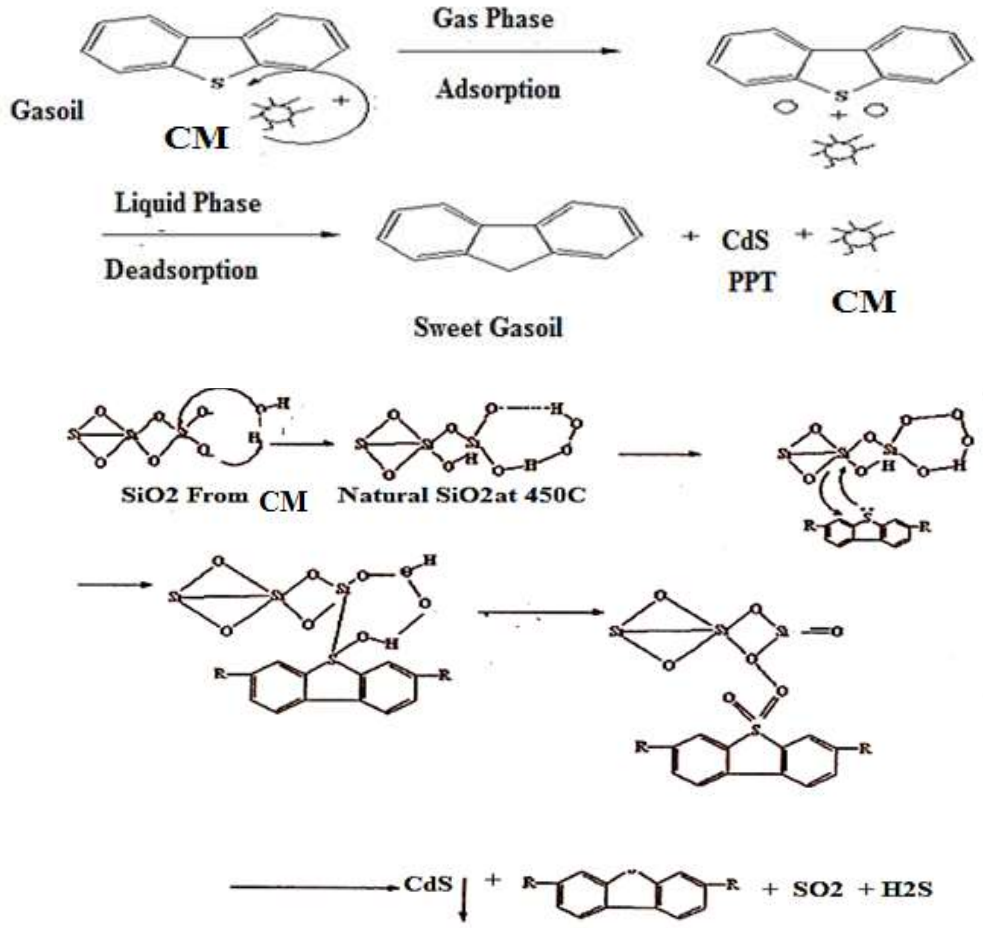


Fig.10. Suggested reaction and mechanism of adsorption desulfurization

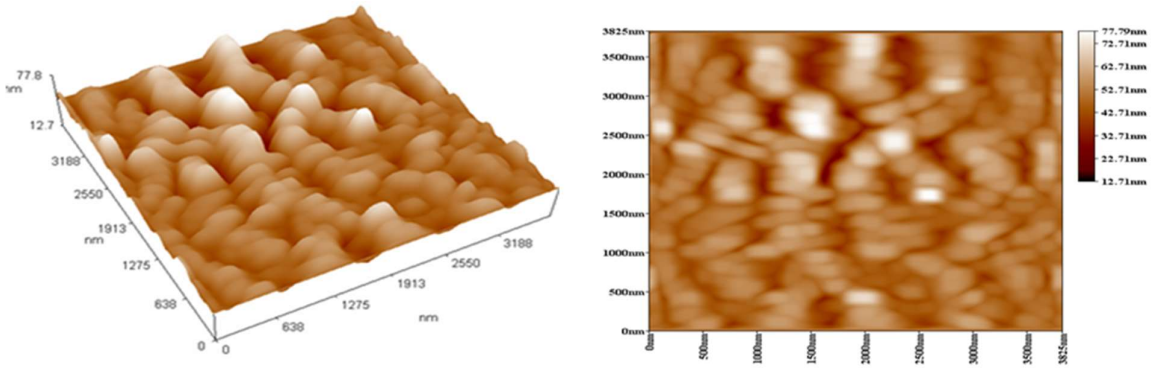


Fig.11. AFM micrographs of Nano A - CM

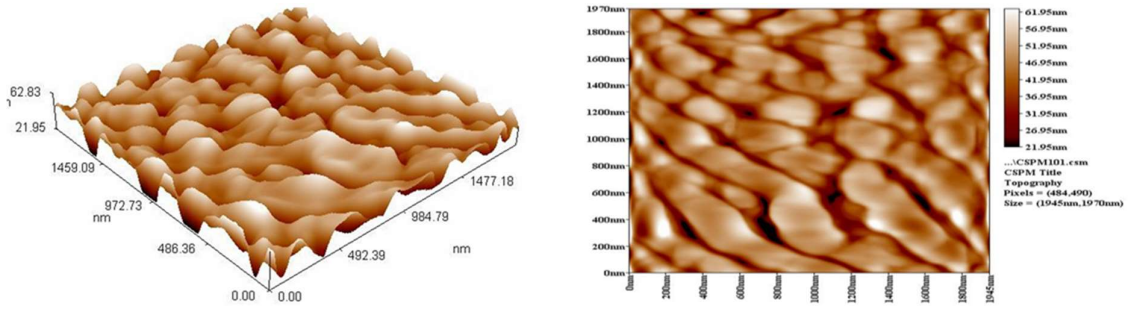


Fig.12. AFM micrographs of Nano B - CM

Reactivity of activated CM catalysts study:

Table.7. Show the reactivity of CM catalysts after uses several times for desulfurization at 450^0C, it reduce when gasoil passes on the MG which reusing, and the S% remove was least than fresh, due to effect of high temperature and carbon accumulations, on other hand the activity of Attapulgite > Bentonite for desulfurization CM. Fig.13 -14

Table.7 catalysts reactivity for sulfur adsorption

CM- Catalyst	Tempt.C^0	First pass. Sulfur % Wt	Second pass. Sulfur % Wt	Third pass. Sulfur % Wt
B	450	0.54	0.82	0.92
A	450	0.47	0.52	0.58

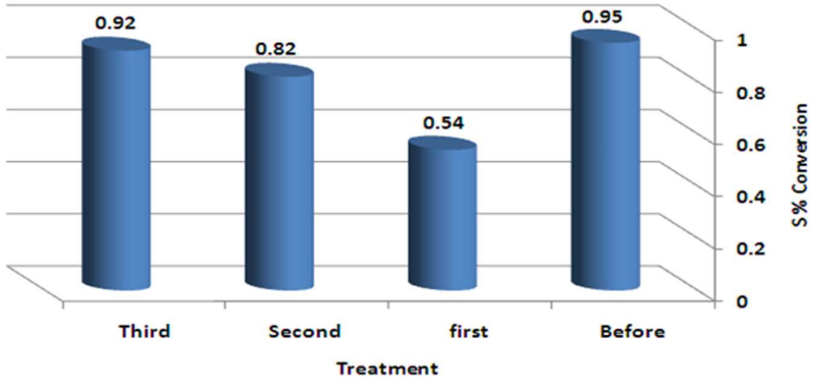


Fig.13 Desulfurization % of activated B –CM with $450C^0$

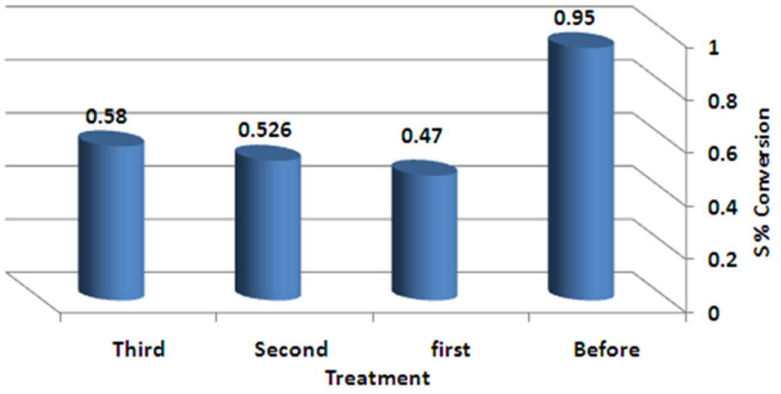


Fig.14. Desulfurization % of activated A – CM with 450C^0

Gas chromatography's (GC) studies:

It is difficult to remove refractory sulfur compounds such as dibenzothiophene (DBT) and their derivatives with one or two alkyl groups which are abundant in gasoline and especially in diesel. The adsorption of dibenzothiophenon (DBT) in Gas-oil onto MG has been studied by Gas chromatography through added small amount of DBT to Gas-oil and follow-up of adsorption to examine the efficiently of desulfurization process. The results show decrease of the DBT% from 5.2124 to 3.1516. Fig.(15 – 18).

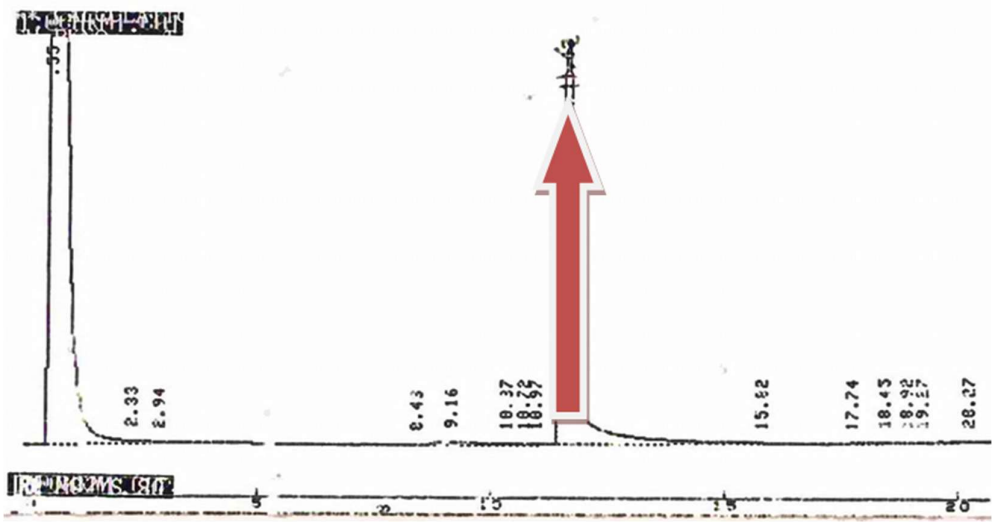


Fig.15. GC profile for DBT (stander) dissolved with hexane

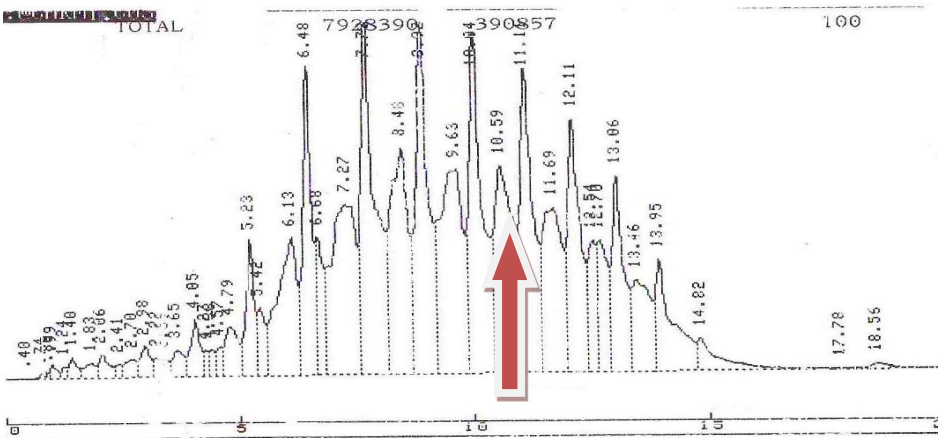


Fig.16. GC profile for virginal Gas-oil

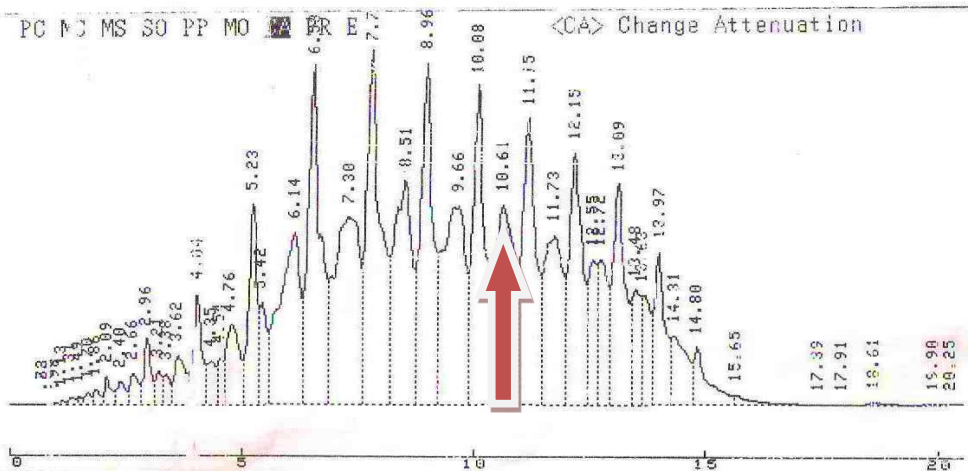
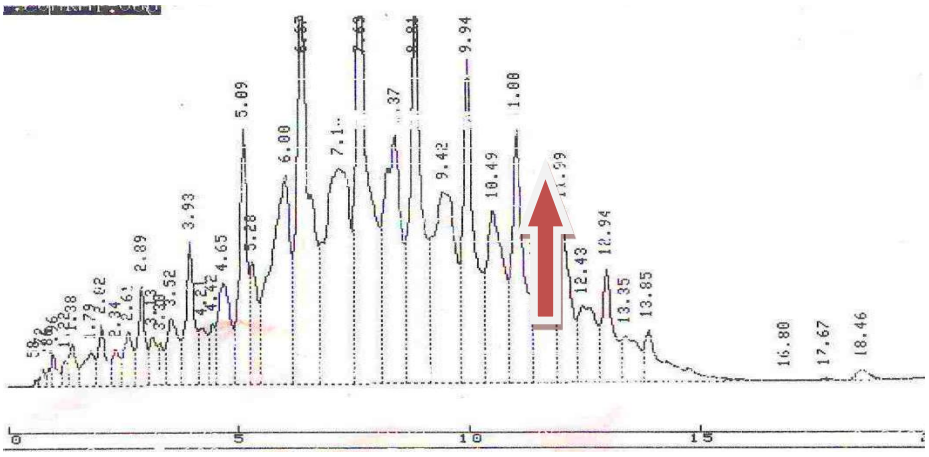


Fig.17. GC profile of adsorption Gas-oil on CM – B



TGA Study

Thermal stability of CM has been studied and carried out with used TGA instrumental for purpose of identifying the stability through high temperatures and determination of the thermal degradation temperature, in other hand to show the optimization temperatures which will could uses of CM as catalyst in different temperatures Fig. (19-20). Show Bentonit at 680^0C thermal

degrade, Attapulgite at 725 ^{0}C which was more stable and is the best absorbent for desulfurization.

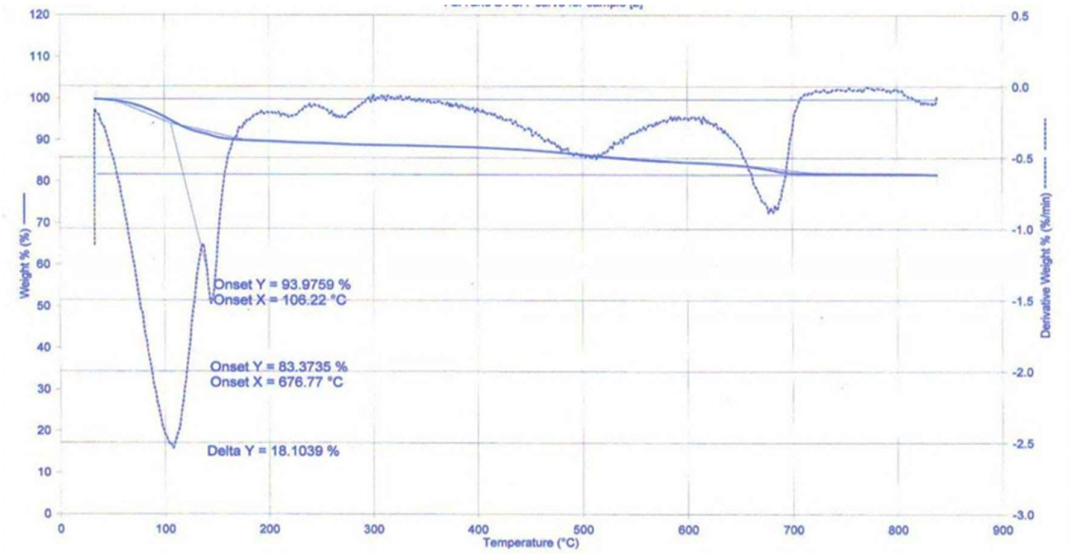
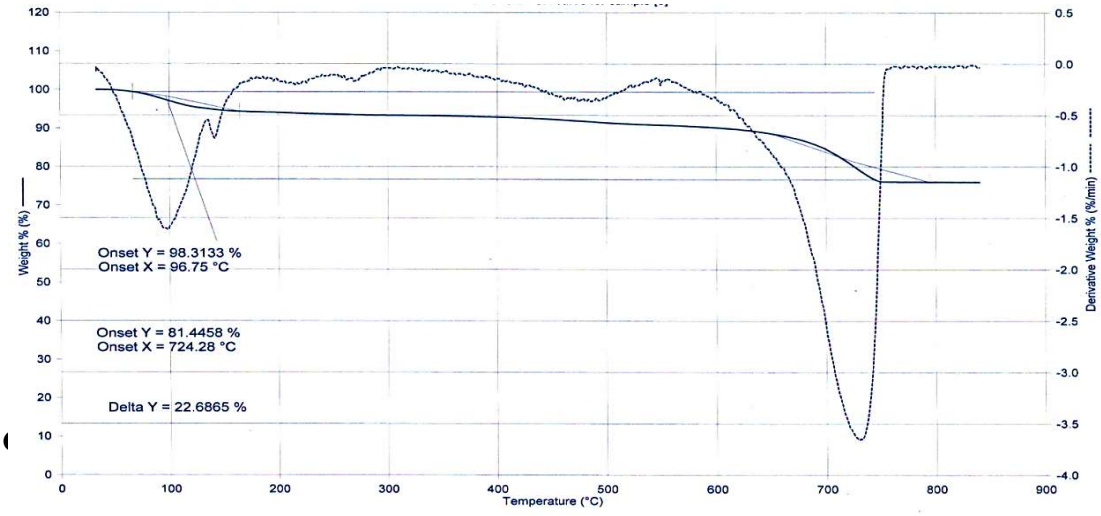


Fig.19 TG and DTGA Curve of CM –B



(c condition at 400,450 and 500C° were successfully, using natural Iraqi CM (Bentonite, Attapulgite). Adsorption efficiently was increased when impregnated with metals oxide (TiO_2,ZnO and MoO_3) with 25%, and more increased using Nano particles size of CM which managed to reduce the sulfur levels from (0.954 – 0.290). Moreover provide simple technique, cheap and ecofriendly. On other hand the efficiently of adsorption for DBT was successfully tested which showed it was bad and difficult for removal from gasoil. Efficiently of Attapulgite was favorite than Bentonit and 450^{0}C is the optimize temperatures in the adsorption desulfurization

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